

WHATEVER HAPPENED TO SILICON CARBIDE

R. B. Campbell
Westinghouse Electric Corporation
P. O. Box 10864
Pittsburgh, PA 15236

Summary

Silicon carbide has been used extensively as an abrasive, but only in the last twenty-five years has its potential as a semiconductor been exploited. The rationale for SiC semiconductor devices is their high temperature performance. Rectifiers, field effect transistors, charged particle detectors, and other devices operate efficiently at temperatures about 800°K.

It is the purpose of this paper to examine the progress made in SiC devices in the 1955-1975 time frame and suggest reasons for the present lack of interest in this unique material. The data given in this paper has been abstracted from previously published work.

Introduction

In the last seventy years, considerable use has been made of the abrasive characteristics of silicon carbide (hereafter SiC); however, only recently were its potentialities as a semiconductor exploited. (1-4) It is the purpose of this paper to discuss SiC devices in the 1955-1975 time frame. Since SiC device properties are intimately connected with its material properties, crystal growth and fabrication techniques will also be discussed. Finally, I will suggest reasons it is no longer considered a viable product for exploitation.

The work discussed in this paper was performed at various industrial and college research laboratories. These programs are no longer active, and there are no known plans or interest in their reactivation.

Physical and Chemical Properties

Silicon carbide exists in the hexagonal (α) and cubic (β) phases with the α phase occurring in a variety of polytypes. The various forms of SiC have the largest energy gaps found in common semiconductor materials, ranging from 2.39 eV (cubic) to 3.33 eV (2H). The bonding of Si and C atoms is basically covalent with about 12% ionic bonding. The structures are temperature stable below 1800°C and thus form a family of semiconductors useful for high temperature electronic devices. Table 1 shows the lattice parameters and energy gap (0°K) for the common polytypes.

Table 1. Lattice Constants and Energy Gap of Common SiC Polytypes

Structure	Lattice Parameters (Å)	Energy Gap (0°K)
2H	a = 3.09 , c = 5.048	3.33
4H	a = 3.09 , c = 10.05	3.26
6H	a = 3.0817, c = 15.1183	3.02
33R		3.01
15R	a = 3.079 , c = 37.78	2.986
21R	a = 3.079 , c = 52.88	2.86
8H		2.80 - 2.90
cubic-3c	a = 4.359	2.39

SiC is inert to nearly all laboratory reagents, and the usual techniques for chemical etching employ molten salt or salt mixtures (NaOH, Na₂O, borax) at temperatures above 600°C. Electrolytic etching, suitable for p-type material and etching with gaseous chlorine near 1000°C, may also be used.

The physical hardness and chemical inertness impose great restraints on device fabrication techniques. Although SiC technology has progressed along the same lines as that of silicon, many techniques had to be developed which were peculiar to SiC and which inevitably made the fabrication more difficult and expensive.

Methods of Preparation

The oldest and perhaps the best known method of SiC crystal growth is the sublimation method. This technique uses the vaporization of a SiC charge at about 2500°C into a cooler cavity with subsequent condensation. Initially the charge formed its own cavity, but more uniform crystals are grown when a thin graphite cylinder is used in the center of the charge. This thin cylinder also reduces the number of nucleations so that fewer but more perfect crystals are grown. The crystals are grown as thin hexagonal platelets, perpendicular to the growth cavity. Doped crystals, containing p-n junctions, can be prepared by adding proper dopants to the ambient during growth. The power rectifiers, to be described later, were prepared by this method.

Other methods of crystal growth are epitaxy, traveling solvent and solution growth.

The hexagonal α phase is grown epitaxially from 1725° to 1775°C with the cubic phase being grown from 1660°C to 1700°C. In both cases, equal molar percentages of CCl₄ and SiCl₄ are used. Polished and etched SiC crystal were generally used as substrates although Ryan and co-workers at Air Force Cambridge Research Laboratory have investigated the growth of SiC onto carbon substrates using the hydrogen reduction of methyltrichlorosilane (CH₃SiCl₃) (called the vapor-liquid-solid growth). At 1500°C, α -SiC whiskers on the order of 5 mm long by 1 mm diameter were grown. These whiskers were of the relatively rare 2H polytype.

SiC crystals have been grown together, and p-n junctions formed by passing a heat zone through two SiC crystals separated by a solvent metal (traveling solvent). The temperature gradient across the thin solvent zone causes dissolution at both solvent-solid interfaces. However, the equilibrium solubility of SiC in the solvent is greater at the hotter interface, a concentration gradient is established. The solute, then, will diffuse across the liquid zone and precipitate onto the cooler crystal. In this way, two dissimilar conductivity type SiC crystals can be grown together.

In the solution growth technique, a small amount of SiC is dissolved in molten Si (or in some cases Fe or Cr). As the melt is slowly cooled, the SiC becomes less soluble; and SiC crystals nucleate and grow in the crucible on prepared graphite substrates. The grown crystals are normally of the β -phase. Improvements in the crucible geometry and cooling rates have led to

cubic crystals up to 4 mm across and 0.1 mm thick. With the use of pure starting materials and extensive degassing, quite pure crystals can be grown; and electron mobilities of 500 cm^2 per volt-sec have been measured.

Device Techniques

The specific device techniques used will vary from device to device, and it is the purpose of this section to discuss fabrication methods in a general manner. In later sections when the individual devices are described, any special techniques required will be discussed.

The mechanical shaping of a hard crystal such as SiC is generally accomplished by scribing and breaking, lapping and polishing, ultrasonic cutting and air abrasive cutting. Boron carbide and/or diamond are used for these purposes since they are the only materials sufficiently hard.

Scribing the crystal with a diamond point and breaking it along the scribe line can also be used. As will be discussed later, a number of field effect transistors were fabricated on a single crystal; and these transistors were separated by scribing. Obviously this is best carried out on a scribing machine.

All of these mechanical shaping operations inevitably leave surface and bulk damage in the crystal. Some studies have indicated that the damage may propagate into the crystal by microcracks to a depth of tens of microns. For optimum device performance this damage must be removed, e.g., by chemical etching.

The etching of SiC using molten salts has been described in detail by Faust in 1959. In his paper, Faust describes the side of the SiC crystal which etches in a rough "wormy" pattern using molten salt on the carbon side and the side where the etch is smooth as the silicon side. This data has also been confirmed by Brack in 1965, using X-ray techniques.

Chang and co-workers studied the diffusion of aluminum into SiC from 1750°C to 2100°C , using both closed tube and open tube flowing gas techniques. Since the SiC crystals will decompose at these temperatures, it was necessary to provide an equilibrium pressure of Si and C vapor species around the crystals during the diffusion process. Griffiths in 1965 and Vodakov et al in 1966 reported further experiments using similar techniques. The activation energy for the diffusion of aluminum into SiC found in these three studies agreed within 5% ($\sim 4.8 \text{ eV}$).

Further refinements in unpublished work by Canepa and Roberts of the Westinghouse R&D Center resulting in junction depletion widths up to $25 \mu\text{m}$ were obtained using a combination of infinite source and finite source diffusion techniques.

Another technique is to use gaseous etching, e.g., Cl_2 at 950°C to 1050°C (Thibault) or $\text{Cl}_2 + \text{O}_2$ at 1000°C (Smith and Chang).

Characteristics of SiC Devices

Figure 1 shows the reverse characteristics of the IV properties of a SiC rectifier prepared by the grown junction method, operating at one ampere and 30°C and 500°C . The forward voltages of these devices, even at 500°C , are always larger than 1 volt (half wave average). Thus far, rectifiers operating up to 10 A have been fabricated, and specially processed low current devices have exhibited reverse capability of

600 PIV. The reverse characteristic of SiC rectifiers generally show a "soft" breakover, rather than the avalanche breakdown sometimes noted in silicon. This is generally attributed to the carrier generation mechanism at the junction and to local areas breaking down at different voltages, so that the total effect is one of gradually increasing reverse current.

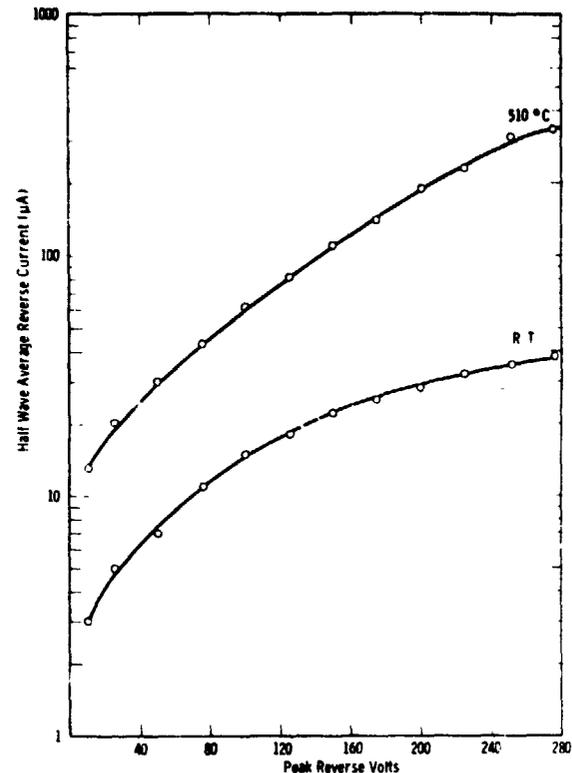


Figure 1. Representative properties of silicon carbide grown junction rectifiers - reverse characteristics

Although very limited life test data have been obtained for these grown junction rectifiers, a few devices have been operated at several amperes for up to 200 hours at 500°C in air, with no change in electrical characteristics. Devices operating at one ampere and using approximately the same encapsulation have been successfully life tested for 1000 hours at 500°C .

The operation of a p-n junction nuclear particle or photon detector depends on the collection of electron-hole pairs produced by the ionizing particle or photon as it passes through the detector. The electron-hole pairs are separated in the junction region, collected, and give rise to a charge or voltage pulse.

Silicon photovoltaic diodes have been developed for the detection of infrared and visible radiation. These diodes exhibit a sharp drop in response as the wavelength of the incident light approaches the ultraviolet region with most detectors showing negligible response below 3000 \AA . This decreasing response is due to the increase in the absorption coefficient with decreasing wavelength. A large absorption coefficient indicates nearly all the light will be absorbed at the surface of the device, and electron-hole pairs generated may be at a great distance from the p-n junction. Thus, surface effects, such as carrier recombination, will decrease the response of the detector.

SiC, with a band gap near 3.0 eV, has an absorption coefficient several orders of magnitude less than that of Si at 4000 Å, and therefore surface effects would not be so important. Detectors have been prepared from SiC, and these devices were found to have a spectral response which were a maximum in the ultraviolet region and which could be shifted by varying the junction depth.

A simple theoretical model was originally derived by Chang and Campbell which quantitatively explained the dependence of the peak wavelength on the junction depth and the depletion width of the diode. Considered in this model were the wavelength and temperature dependences of the absorption coefficient in SiC below the band edge. An approximation was made that at the peak response wavelength, the total number of electron-hole pairs generated in the depletion layer is a maximum for a given intensity of transmitted radiation at the surface.

Figure 2 shows the variation of peak response wavelength calculated from this model. The curves are shown for values of the effective depletion width (w) from $w = 1$ micron to $w = 10$ microns.

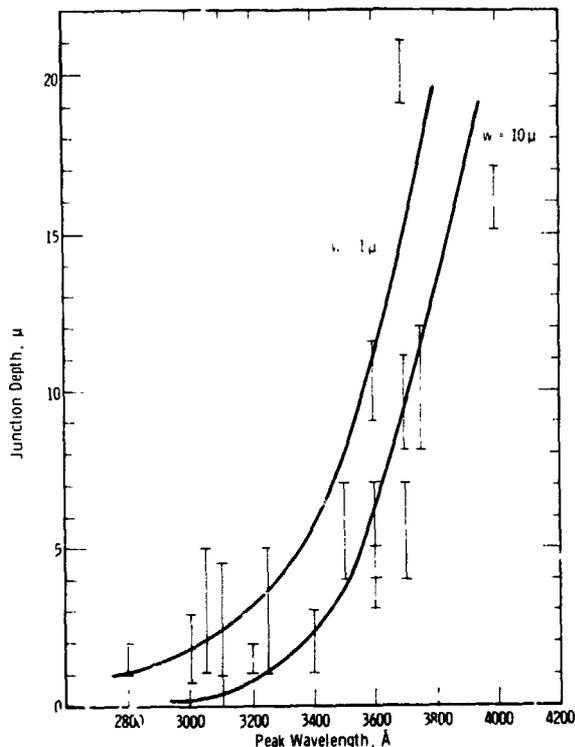


Figure 2. Peak spectral response of silicon carbide junction diode as a function of junction depth (after Campbell and Chang)

In addition to these photon detectors, SiC diode structures, specially prepared with graded junctions, have been used to detect alpha particles; and with the addition of a conversion layer, thermal neutrons have been counted.

The fission products of U-235 irradiated with thermal neutrons are not unique but have a distribution with two peaks occurring in the fission product mass distribution curve. The total energy liberated is 157 MeV with peaks at 66 and 91 MeV. Figure 3 shows a comparison of the alpha and fission product spectra for a SiC diode. The fission products spectra

are very close to those predicted from the α -particle response taking into account the different distribution in the incident energy. The SiC diode, which had a peaked α -spectra, also shows a peak fission product spectra; in fact, the fission spectra of the diode resolves the double peaks.

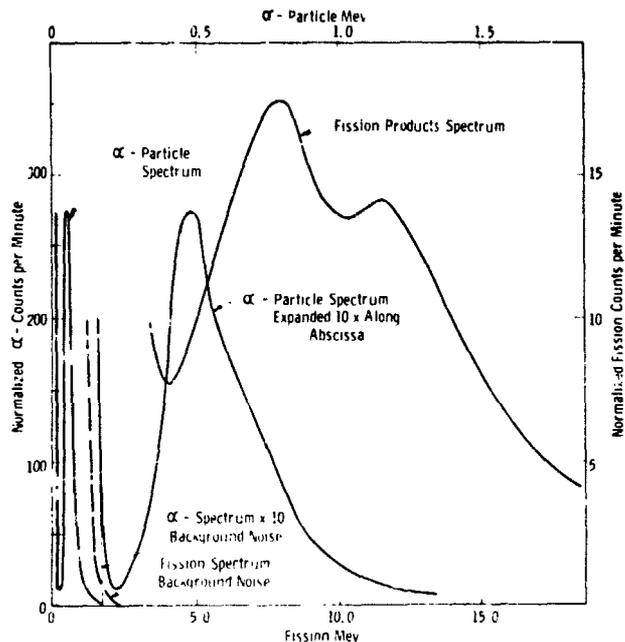


Figure 3. Comparison of alpha particle and fission fragment counting of silicon carbide junction diode (after Canepa et al)

Tunnel diodes in SiC can be made by forming a heavily doped alloyed junction in either n- or p-type degenerate SiC crystals, using a very fast alloying cycle similar in principle to that originally used to produce Ge tunnel diodes. Degenerate n-type SiC can be grown readily with heavy nitrogen doping. The p-type degeneracy in SiC cannot be established until the uncompensated acceptor level approaches $10^{20} - 10^{21} \text{ cm}^{-3}$, which has not been achieved.

An operable SiC tunnel diode was reported by Kutz in 1964. The junction was formed by alloying Si in a nitrogen-containing atmosphere to very heavily Al-doped α -SiC crystals ($4.5 \times 10^{20} - 9 \times 10^{20}$ uncompensated acceptors cm^{-3}). The highest peak-to-valley current ratio achieved was 1.37 at room temperature, but negative resistance was observed at temperatures as high as 500°C. The peak voltage is unusually high, approximately 0.9V and 24°C. Figure 4 shows the IV characteristics of a SiC tunnel diode at several temperatures.

The channel dimensions and other device dimensions in a SiC junction gate field effect transistors are quite small due to the low carrier lifetime and correspondingly short diffusion lengths. Thus, the fabrication of these devices require photolithographic techniques. Using a self-masked diffusion process and gaseous etching (see Figure 5), Chang et al fabricated SiC FET's which exhibited current gain from room temperature to 500°C.

A silicon carbide thermistor was described by Campbell in 1973. This device takes advantage of the exponential decrease in resistance of a SiC junction

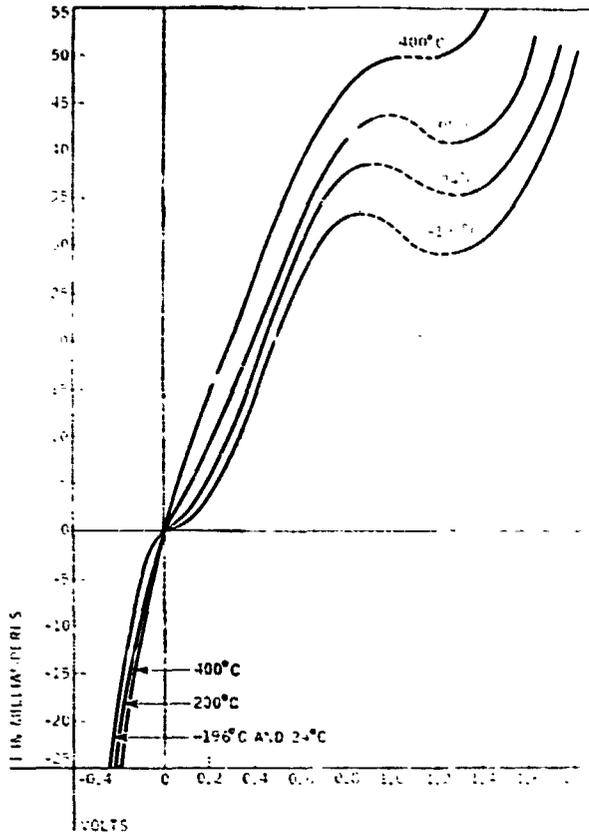


Figure 4. IV characteristics of silicon carbide tunnel diode from -196°C to 400°C (after Rutz)

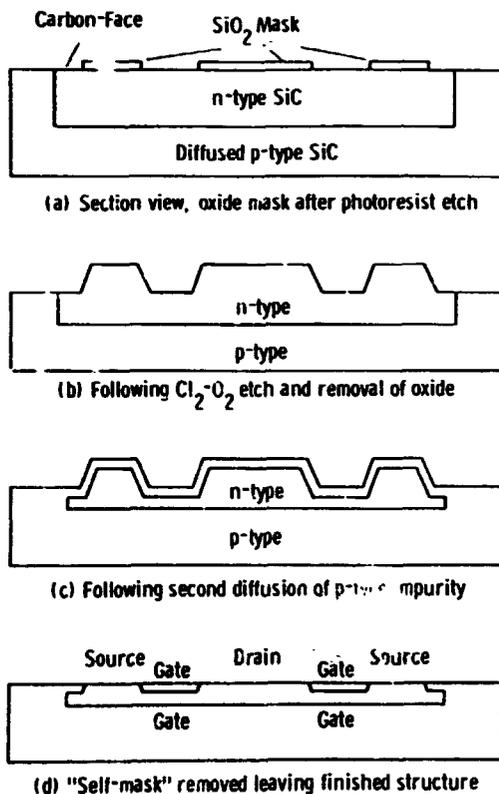


Figure 5. Self-masked diffusion technique

with temperature. Since this resistance changes by an order of magnitude for every 100°C temperature change, a change of a few tenths of a degree is easily detected. Prototype devices have been operated several thousand hours (with frequent cycling) without degradation.

Conclusions

Thus far I have given a brief outline of SiC semiconductor devices and methods for their fabrication. The data given show that SiC devices are feasible and have properties that should be of interest to several high technology fields. The question then arises: Why is there so little interest in this material today, and why are there no SiC devices currently in use?

I believe there are three specific reasons for this. First, in the later 1960's there was a decline in corporate and Government R&D funding due to economic conditions. At this time, SiC had not carved out its niche in the semiconductor device market and thus was a prime candidate for any cutback. A second, somewhat related, cause was the disappearance of the small market where SiC devices did have a chance to make an impact. These were high technology areas such as near sun space missions, supersonic and hypersonic aircraft, etc. When these markets disappeared, much of the interest in SiC also disappeared. Finally, the fabrication techniques for SiC devices (including growth methods) did not improve appreciably in the twenty years under question. This lack of progress may have been due to misplaced emphasis in device programs, but the net result was that the fabrication techniques for SiC devices improved only slightly in this time span.

Now, where do we go from here? I see no viable market for SiC semiconductor devices in the near future. Improved Si devices, better insulation, improved circuit design all mitigate against any extensive use of SiC devices. This may be viewed as an unfortunate circumstance to many of us who were professionally and emotionally involved with this interesting material for a number of years.

Acknowledgments

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References

The following four references contain all the work discussed in this paper.

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